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(54) Catalyst material comprising platinum alloy supported on carbon

(57) An electrocatalytic material comprises an alloy of platinum with another element, supported on a conductive carbon support, the metal area of the alloy being greater than 75 m²/gPt, and at a useful platinum loading, is especially suitable for use in phosphoric acid fuel cells, and demonstrates unexpectedly high stability at the high metal areas obtained. This material is produced by supplying a basic solution of compounds of platinum and one or more alloying elements onto the carbon support and reducing and heat treating the support carrying the compounds so as to form the platinum alloy. Suitable alloying elements are Ti, Cr, Mn, Fe, Co, Ni, Cu, Zr and Mo. The catalyst may have a BET-surface area of less than 1000m²/gm. The reduction may be carried out in the liquid phase by adding a reducing agent to the slurry after deposition; drying the slurry and then reducing using a gas phase reducing agent. Alternatively reduction and heat treatment may take place in a single step.

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IMPROVED CATALYST MATERIAL

This invention concerns an improved catalyst material, more especially it concerns a catalyst material of particular interest for fuel cells, containing a platinum alloy.

In the art of fuel cells, there have been very many proposals for the production of electrocatalysts which are used to coat one or both of the electrodes. It is useful to recall that in a fuel cell, a fuel, which may be hydrogen, a hydrocarbon or an oxygen-containing fuel such as methanol, is oxidised at a fuel electrode (anode) and oxygen is reduced at the cathode. An electrolyte contacts the electrodes, and may be alkaline or acidic.

The phosphoric acid fuel cell (PAFC) is the type of fuel cell closest to commercialisation and there are a number of demonstration units, especially in Japan, where there are considerable economic and environmental pressures to reduce imports of hydrocarbon fuels and to cut polluting emissions from power generation. Many people consider that fuel cells are, however, unlikely to get beyond the demonstration stage unless there are overwhelming political or environmental reasons, because the power output is too low for the capital costs involved. In the PAFC, power output is limited in part by the activity of the cathode catalyst. Increasing cathode catalyst activity can result in higher power density at the same efficiency. The capital cost per unit of power is therefore reduced in proportion to the increase in performance. Because the cost of the cathode catalyst is only a fraction of the cost of the fuel cell stack, increasing the power density of the stack reduces the capital cost per unit power out of all proportion to the value of the catalyst per se. It is therefore widely recognised that a cathode catalyst with improved performance would have great value in reducing overall capital cost per unit power even in light of increased cost of the catalyst itself.

It has been proposed, eg in USP's 3,354,060 and 3,468,717 (Standard Oil), USP 4,186,110 (United Technologies), GB 2,190,537A and 2,185,347A (Nippon Engelhard), to use alloys of platinum with base metals, deposited on a conductive carbon substrate, as electrode materials in acid electrolyte fuel cells. It is

suggested in this prior art that such alloys, which include within their meaning solid solutions and intermetallic compounds, have greater activity per unit weight compared to unalloyed platinum. It is well known that increasing the effective surface area of the catalyst increases catalyst performance. There are several ways in which this may be achieved. Increasing the amount of supported catalyst in the electrode will increase the total effective surface area of active catalyst material. However, this increases the thickness of the fuel cell electrode, increasing internal resistance, thus reducing the overall benefit. Alternately, the active area per unit weight of metal supported on the carrier may be increased. This allows for an increase in the total amount of active surface area in the electrode without increasing the amount of catalyst or the electrode thickness. This is achieved by increasing the dispersion of the active metal. It would therefore be very advantageous to make supported Pt alloy catalysts with higher metal dispersions (active area per unit weight of metal) than is currently practised.

It has become accepted in the fuel cell catalyst art that a "standard" catalyst formulation comprises approximately 7 to 11% by weight platinum, by itself or as an alloy, on carbon. The state of the art Pt alloys of this type typically have dispersions of 45 to 65 m²/g as measured by ECA as defined below. The prior art contains many statements concerning the desirability of high surface area or dispersion. There are many examples of 10 wt% Pt alloys with active surface areas in the range indicated above and of

unalloyed Pt catalysts with significantly higher surface areas. There are, however, no instances of Pt alloy catalysts being exemplified with active areas significantly greater than 65 m²/g Pt in a convincing manner.

In particular should be mentioned the techniques described by Petrow and Allen, USP 4,044,193 for making highly dispersed unalloyed Pt catalysts supported on conductive carbon supports. These however do not show the superior performance found with Pt alloy catalysts for application as PAFC cathode catalysts. We are not aware that any alloy catalyst having a high dispersion as measured by ECA and high activity has been described. There remains a need for an electrode material having the high electrocatalytic activity of Pt alloys, with high active metal dispersion and supported on a stable non-corroding carbon support which is capable of a relatively long effective life. It is an aim of the present invention to satisfy these criteria.

References herein to ECA (Electrochemical Area), are to areas determined in accordance with the method described in S. Gilman, J. Electroanal. Chem., 7, 1964, 382. This method is based on the use of cyclic voltammetry to deposit and strip off a monolayer coverage of hydrogen on the active catalyst surface at potentials close to hydrogen evolution. A three compartment electrochemical cell is used and hydrogen adsorption is measured on a fully wetted electrode comprising the electrocatalyst material. The charge associated with hydrogen adsorption is measured and

using the relationship $1 \text{ cm}^2 \text{ Pt} = 210 \mu\text{C}$ (C-Coulomb), the electrochemical area of the catalyst in terms of m^2/g Pt is determined.

Hereinafter, we shall use the terms "activity" and "stability" as defined below. Hydrophobic electrodes are prepared by mixing the catalyst with PTFE, applying to a wetproofed graphite paper and sintering as is usually practised in the art. Activity is measured in a cathodic half cell using air and oxygen as reactants. The measurements are made at 180°C , atmospheric pressure and in 100% phosphoric acid as electrolyte. Activity is a measure of the oxygen reduction ability per unit weight of the platinum present, and is measured by the current flow through the electrode at an IR (Internal Resistance)- free potential of 900 mV, versus a Dynamic Hydrogen Electrode (DHE), with oxygen as the reactant, and is expressed in terms of milliamps per milligram of platinum present.

During prolonged use under fuel cell operating conditions the active catalyst particles have a tendency to coalesce, either by surface migration or dissolution/re-precipitation. This process, known as sintering, causes a reduction in effective surface area and hence in activity. To provide an indication of the resistance of the catalyst to these detrimental sintering processes a "stability" test has been developed. A catalyst sample is thoroughly dispersed in 100% phosphoric acid, and is

maintained at a temperature of 180°C for 72 hours. An electrode is then prepared and ECA and activity measured as above and compared to the fresh catalyst.

The present invention provides a novel electrocatalytic material comprising an alloy of platinum, supported on a conductive carbon support, the ECA of the alloy being greater than 75 m²/g platinum and at a useful platinum loading. Preferably the BET surface area of the catalyst material is less than 1000m²/g, more preferably less than 300m²/g, and especially less than 120m²/g, particularly if the material is for use in phosphoric acid fuel cell cathodes. Preferably the alloying element(s) are selected from the transition metals, more preferably from Groups IVB, VIB, VIIB, VIII and IB of the Periodic Table in "Handbook of Chemistry and Physics", 64th Edition, CRC Press. Even more preferably, the alloying elements are selected from one or more of Ti, Cr, Mn, Fe, Co, Ni, Cu, Zr, and Hf, especially one or more of Cr, Mn, Co and Ni. Preferably the atomic ratio of platinum to the alloying element(s) is in the range of 80:20 to 20:80, more preferably in the range of 65:35 to 35:65, especially approximately 50:50. These materials have an ECA greater than 75 m²/gPt, more preferably greater than 80 m²/g Pt, especially greater than 90 m²/gPt, and particularly greater than 100m²/g Pt. Useful platinum loadings are generally accepted as being greater than 5 wt% Pt, and suitable loadings are in the range 7.5 to 20 wt%, preferably 7.5 to 15 wt% Pt. It is believed that this combination of properties has not previously been accessible by prior art techniques and that the material is novel.

The invention further provides a method for the manufacture of a material as defined above, which method comprises a depositing from basic solution, compounds of the desired platinum group metal and desired alloying element(s) onto a conductive carbon electrocatalyst support, and reducing and heat treating the support carrying metal compounds to obtain an alloy of platinum and said at least one other element, having an ECA in excess of $75\text{m}^2/\text{g}$ of platinum.

Suitable conductive carbon supports are commercially available or may be prepared specifically for this application. Preferred carbons are the oil furnace carbon blacks or acetylene blacks. They may be used as prepared commercially, or specifically treated to increase their graphitic character.

In the method of the invention, it is preferred to dissolve the compounds of the metals in water and to add these either simultaneously or sequentially to an aqueous basic slurry of the carbon, conveniently depositing the platinum group metal firstly. Desirably, the carbon is slurried in water and the slurry is rendered alkaline, for example by the addition of sodium bicarbonate which also serves as a buffer. Suitable metal compounds are, for example chloroplatinic acid for platinum, and readily soluble salts for the base metals, such as chlorides or nitrates. For the purpose of safety, care should be taken when adding chloroplatinic acid in particular, but also the other compounds, to avoid excessive gas evolution and eruption of the material from the vessel.

The deposited compounds are required to be reduced to the metal, so that they may form an alloy, and this may be accomplished in a number of ways. The reduction may be carried out in the liquid phase, by adding a reducing agent, such as hydrazine, formaldehyde or formic acid, to the slurry after deposition. In another reduction method, the slurry is dried and reduced using a gas phase reducing agent, which is suitably hydrogen, which may be diluted with an inert gas such as nitrogen. These particular reduction methods are followed by a heat treatment, for example to 600 to 1000°C. Another variant of the process permits reduction and heat treatment to take place in a single step; heating to a temperature of approximately 600 to 1000°C under an inert gas or in a reducing atmosphere for an appropriate time of approximately one hour has been successful in tests. There are many methods of heating in order to form the alloy, and it is possible to alter the time and temperature profiles in order to achieve particular alloy characteristics. It is preferred to avoid temperatures significantly above 1000°C if the material is heated for any significant time, since sintering and loss of surface area may occur. Care should be taken with carbon, carrying deposited platinum or compounds thereof, since it tends to be pyrophoric; it is preferably kept under an inert atmosphere or at least denied access to air or oxygen except when at approximately room temperature or below.

The materials of the invention have particular utility as the active component in the oxygen reduction electrode of an acid electrolyte fuel cell. Accordingly, the invention encompasses the use of the materials. The materials may be used in conventional manner, which generally involves dispersing the material in a suspension of PTFE, coating a substrate such as PTFE - wet proofed graphite paper with the dispersion, and sintering the coated substrate. The invention further includes a fuel cell, especially a phosphoric acid fuel cell, using an electrode according to the invention.

Although the material according to the invention has particular application in PAFC, and is described herein in detail with reference to this use, it is clear to us that the materials have uses in other fuel cells or for other applications.

The invention will now be particularly described in the following examples, which are to be regarded as illustrative and not limiting. Each of the exemplary catalysts was made into test electrodes following the methods outlined above. Measurements of ECA and activity were taken to characterise the properties of the various catalysts. These results are presented in the Table.

EXAMPLE 1 (Comparativ Exampl - Pt/Co/Cr, 10wt% Pt)

A method following that described by Luczak and Landsman (USP 4,447,506) was used. A conventional high surface area 10.3 wt% Pt catalyst was prepared on Shawinigan carbon black. 48.6 g of this material was slurried in demineralised water. To the slurry was added 0.905 g of Co as $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.538 g of Cr as $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. The slurry was vacuum dried at 80°C, then heat treated at 930°C in a flowing nitrogen atmosphere for 60 minutes to form the alloy. The resulting catalyst comprised 10 wt% Pt, 1.8 wt% Co, and 1.08 wt% Cr with an atomic ratio of 50:30:20 Pt:Co:Cr.

EXAMPLE 2 (Comparative Example - Pt/Ni, 10 wt% Pt)

A Pt/Ni alloy catalyst was prepared at 10 wt% Pt loading as follows: 43.5g Shawinigan acetylene black was added to 2,000 cm³ demineralised water and stirred for 15 minutes to produce a homogeneous slurry. 17.22g sodium bicarbonate was added to the slurry and stirred for 5 minutes. The slurry was raised to 100°C and maintained at the boil for 30 minutes. A solution of 5.0g platinum as chloroplatinic acid, in 60 cm³ demineralised water, was added to the slurry over 5 minutes. The slurry was boiled for 5 minutes. A solution of 1.51g nickel, as the nitrate salt ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), in 50 cm³ demineralised water was added over 10 minutes. The slurry was boiled for two hours. 3.9 cm³ of formaldehyde solution, diluted to 38 cm³ was added over ten minutes. The slurry was boiled for a further 60 minutes and then

filtered to remove the supernatant liquid and washed with demineralised water to remove the soluble chloride species. The chloride free filter cake was vacuum dried at 80°C until the moisture content was less than 2%. The material was then heated to a temperature of 930°C in a flowing nitrogen atmosphere and maintained at this temperature for 60 minutes to form the alloy. This gives a catalyst with a composition of 10 wt% Pt, 3.0 wt% Ni and a Pt:Ni atomic ratio of 50:50.

EXAMPLE 3 (Example - Pt/Mn, 10 wt% Pt)

The method as described in Example 2 was used to prepare a Pt/Mn catalyst at 10 wt% Pt loading. The base metal solution comprised 2.253g of Mn as $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ dissolved in 150 cm³ demineralised water. The quantity of Pt used was 8.0g Pt as CPA, and that of carbon was 69.75g to give a catalyst with composition of 10 wt% Pt and 2.8 wt% Mn with an atomic ratio of 50:50 Pt:Mn. However, no formaldehyde was added during the catalyst preparation.

EXAMPLE 4 (Example - Pt/Ni, 10 wt%)

The method as described in Example 2 was used to prepare a Pt/Ni catalyst at 10 wt% Pt loading, except that no formaldehyde solution was added during the catalyst preparation.

EXAMPLE 5 (Example - Pt/Ni, 10wt% Pt)

The method as described in Example 2 was used to prepare a Pt/Ni catalyst at 10 wt% Pt loading, except that the carbon support was Cabot Vulcan XC72R furnace black.

EXAMPLE 6 (Example - Pt/Ni, 10 wt% Pt)

The method as described in Example 2 was used to prepare a Pt/Ni catalyst at 10 wt% Pt loading, except that the carbon support was Cabot Vulcan XC72R furnace black and no formaldehyde solution was added during the catalyst preparation.

EXAMPLE 7 (Example - Pt/Ni, 15 wt% Pt)

The method as described in Example 6 is used to prepare a Pt/Ni catalyst at 15 wt% Pt loading, except that all reagent quantities were altered in proportion to give a catalyst with a composition of 15 wt% Pt and 4.5 wt% Ni.

EXAMPLE 8 (Example - Pt/Co/Cr, 10 wt% Pt)

The method as described in Example 4 is used to prepare a Pt/Co/Cr catalyst at 10% Pt loading, except that the alloying elements added comprised 9.1g Co as $\text{Co}(\text{Cl})_2 \cdot 6\text{H}_2\text{O}$ and 5.35g Cr as $\text{Cr}(\text{Cl})_3 \cdot 6\text{H}_2\text{O}$, using 50 g of Pt as CPA and 436g of Shawinigan carbon support, and that the dried catalyst was reduced at 200°C in

flowing 5% H_2 /95% N_2 for 60 minutes immediately prior to heat treatment. The resulting catalyst comprises 10 wt% Pt, 1.82 wt% Co, and 1.07 wt% Cr with an atomic ratio of 50:30:20, Pt:Co:Cr.

EXAMPLE 9 (Example - Pt/Ni, 10 wt% Pt)

The method as described in Example 4 is used to prepare a Pt/Ni catalyst at 10% Pt loading, except that the dried catalyst was reduced at 200°C in flowing 5% H_2 /95% N_2 for 60 minutes immediately prior to heat treatment. The resulting catalyst comprises 10 wt% Pt and 3.0 wt% Ni with an atomic ratio 50:50, Pt:Ni.

EXAMPLE 10 (Example - Pt/Ti, 10 wt% Pt)

A Pt/Ti alloy catalyst was prepared at 10 wt% Pt loading as follows: 54g Shawinigan acetylene black was added to 3,000 cm³ demineralised water and stirred for 30 minutes to produce a homogeneous slurry. 18.0g sodium bicarbonate was added to the slurry and stirred for 5 minutes. The slurry was raised to 100°C and maintained at the boil for 30 minutes. A solution of 6.0g platinum as chloroplatinic acid 0.48 g of Ti as $TiCl_3$, in 90 cm³ demineralised water, was added to the slurry over 30 minutes. The slurry was boiled for 90 minutes. 300 cm³ of 1% formaldehyde solution was added over ten minutes. The slurry was boiled for a further 60 minutes and then filtered to remove the supernatant liquid and washed with demineralised water to remove the soluble

chloride species. The chloride free filter cake was dried at 100°C until the moisture content was less than 2%. The material was then heated to a temperature of 850°C in a flowing nitrogen atmosphere and maintained at this temperature for 60 minutes to form the alloy. This gives a catalyst with a composition of 10 wt% Pt, 0.8 wt% Ti and a Pt:Ti atomic ratio of 75:25.

EXAMPLE 11 (Example - Pt/Hf, 10 wt% Pt)

The method as described in Example 10 was used in analogous manner to prepare a Pt/Hf catalyst at 10 wt% Pt loading, except that the alloying element used was hafnium. The catalyst composition was 10 wt% Pt and 2.0 wt% Hf with an atomic ratio of 75:25, Pt:Hf.

EXAMPLE 12

The catalyst of Example 1 after the stability test.

EXAMPLE 13

The catalyst of Example 2 after the stability test.

EXAMPLE 14

The catalyst of Example 6 after the stability test.

TABLE

EXAMPLE NO.	FORMULATION	PT LOAD WT%	ECA (m ² /gPt)	ACTIVITY (mA/mgPt)
1	Pt/Co/Cr	10	41	36
2	Pt/Ni	10	63	50
3	Pt/Mn	10	90	47
4	Pt/Ni	10	106	66
5	Pt/Ni	10	77	46
6	Pt/Ni	10	80	70
7	Pt/Ni	15	83	NA
8	Pt/Co/Cr	10	76	65
9	Pt/Ni	10	76	65
10	Pt/Ti	10	80	60
11	Pt/Hf	10	89	54
12	Pt/Co/Cr	10	29	30
13	Pt/Ni	10	57	40
14	Pt/Ni	10	77	61

It can readily be seen that the prior art catalysts as exemplified in Examples 1 and 2 show ECA's typical of state of the art catalysts. The examples of the material of the invention, on the other hand, consistently demonstrate extraordinarily high ECA's above 75 m²/g, together with improved oxygen reduction activity, as would be predicted by the ECA data.

From consideration of Examples 12 through 14 it is clear that the stability of the Example according to the invention (Example 14) as assessed by the change in ECA and activity after the sintering treatment of the stability test, is surprisingly superior to the Examples of the conventional art (Examples 12 and 13). This is a surprising result in light of the conventional wisdom that high ECA samples will have reduced stability.

CLAIMS

1. An electrocatalytic material comprising an alloy of platinum supported on a conductive carbon support, and the ECA of the alloy being greater than 75 m²/g Pt and at a useful platinum loading.
2. A material according to Claim 1, in which the alloying element is one or more selected from Groups IVB, VIB, VIIB, VIII and IB.
3. A material according to Claim 2, in which the alloying element is one or more of Ti, Cr, Mn, Fe, Co, Ni, Cu, Zr and Hf.
4. A material according to Claim 3, in which the alloying element is one or more of Cr, Mn, Co and Ni.
5. A material according to any one of the preceding Claims in which the BET surface area of the catalyst is less than 1,000 m²/g.
6. A material according to Claim 5, in which the BET surface area of the catalyst is less than 300 m²/g.
7. A material according to Claim 6, in which the BET surface area of the catalyst is less than 120 m²/g.

8. A material according to any one of the preceding Claims, in which the atomic ratio of Pt to the alloying element(s) is in the range of 80:20 to 20:80.

9. A material according to Claim 8, in which the atomic ratio of Pt to the alloying element(s) is in the range of 65:35 to 35:65.

10. A material according to Claim 9, in which the atomic ratio of Pt to the alloying element(s) is approximately 50:50.

11. A material according to any one of the preceding Claims, in which the loading of platinum metal is in the range 7.5 to 20 wt%.

12. A material according to Claim 11, in which the loading of platinum metal is in the range 7.5 to 15 wt%.

13. A material according to any one of the preceding claims, in which the ECA of the alloy is greater than 80 m²/g Pt.

14. A material according to claim 13, in which the ECA of the alloy is greater than 90 m²/g Pt.

15. A material according to claim 14, in which the ECA of the alloy is greater than 100 m²/g Pt.

16. A material according to Claim 1, substantially as hereinbefore described.

17. A method for the production of an electrocatalytic material according to any of the preceding claims, comprising depositing from basic solution compounds of platinum and one or more alloying elements, onto a conductive carbon electrocatalyst support, and reducing and heat treating the support carrying the compounds to obtain an alloy of platinum and at least one other element, of ECA in excess of $75\text{m}^2/\text{g}$ of platinum, and at a useful platinum loading.

18. A method according to claim 17, wherein the compounds are dissolved in water, and are added to an aqueous basic slurry of the carbon.

19. A method according to claim 17, substantially as hereinbefore described.

20. The use of the material according to any one of claims 1 to 16, as an electrocatalyst in a fuel cell.

21. A catalysed electrode comprising a material according to any one of claims 1 to 16.

22. A fuel cell comprising a catalysed electrode according to claim 21.

23. A fuel cell according to claim 22, wherein the said catalysed electrode is the cathode and the electrolyte is phosphoric acid.